Evaluation of Pesticide residues in fruits and vegetables from Algeria

Article *in* Food Additives and Contaminants: Part B Surveillance · January 2017

DOI: 10.1080/19393210.2016.1278047

6 authors, including:

Samira Mebdoua
Université de Bouira

Mohamed Lazali
Université Djilali Bounaama de Khemis Miliana

Sidi Mohamed Ounane
Ecole Nationale Supérieure Agronomique

Sihem Tellah
Ecole Nationale Supèrieure Agronomique ENSA Algèrie

Taylor & Francis
Taylor & Francis Group

Food Additives & Contaminants: Part B
Surveillance

ISSN: 1939-3210 (Print) 1939-3229 (Online) Journal homepage: http://www.tandfonline.com/loi/tfab20

Evaluation of pesticide residues in fruits and vegetables from Algeria

Samira Mebdoua, Mohamed Lazali, Sidi Mohamed Ounane, Sihem Tellah, Fahima Nabi & Ghania Ounane

FOOD ADDITIVES & CONTAMINANTS: PART B, 2017
http://dx.doi.org/10.1080/19393210.2016.1278047

Taylor & Francis
Taylor & Francis Group

Evaluation of pesticide residues in fruits and vegetables from Algeria

Samira Mebdoua[a], Mohamed Lazali[b], Sidi Mohamed Ounane[a], Sihem Tellah[a], Fahima Nabi[a] and Ghania Ounane[a]

[a]Laboratoire d'Amélioration Intégrative des Productions Végétales, Ecole Nationale Supérieure Agronomique, Alger, Algérie; [b]Faculté des Sciences de la Nature et de la Vie et des Sciences de la Terre, Université Djilali Bounaama, Khemis Miliana, Algérie

ABSTRACT

A total of 160 samples of 13 types of fresh fruits and vegetables from domestic production and import were analysed to detect the presence of pesticide residues. Analysis was performed by multi-residual extraction followed by gas chromatography–mass spectrometry. In 42.5% of the tested samples, no residues were found and 12.5% of samples contained pesticide residues above maximum residue limits. Risk assessment for long-term exposure was done for all pesticides detected in this study. Except chlorpyrifos and lambda-cyhalothrin, exposure to pesticides from vegetables and fruits was below 1% of the acceptable daily intake. Short-term exposure assessment revealed that in seven pesticide/commodity combinations, including three pesticides (chlorpyrifos, deltamethrin and lambda-cyhalothrin), the acute reference dose had been exceeded.

ARTICLE HISTORY
Received 21 August 2016
Accepted 26 December 2016

KEYWORDS
Pesticide residues; fruits; vegetables; long-term exposure; short-term exposure

Introduction

Fruits and vegetables constitute an important part of our daily diet. In fact, these agricultural products are important sources of carbohydrates, vitamins, trace minerals and antioxidants and have also a central role in a balanced diet (Karmas & Harris 1988; Prodanov et al. 2004). However, they can contain toxic pesticide residues resulting from agricultural practices related to these crops, as the use of pesticides in fruit and vegetable cultures is a common practice and it is indispensable for intensive production. In a context of good agricultural practices (GAP), residues of pesticides in food should not exceed the maximum residue limits (MRLs) in order not to violate legislation.

MRLs are based on GAP data for production of food commodities and are not toxicological limits as such. Exceedance of MRLs is a strong indicator of violation of GAP (Nasreddine & Parent-Massin 2002). Because most of the fruits and vegetables are eaten unprocessed, they are the main source of pesticide residues intake for consumers (Szpyrka et al. 2015). Human intake of pesticide residues in food commodities can be higher than intake of these substances in water consumption and air inhalation (Juraske et al. 2007). Therefore, regular monitoring of residue levels in fruits and vegetables is required to protect consumer's health.

Published data on pesticide residues in fruits and vegetables consumed in Algeria are scarce, if any, and systemic investigation is needed to verify the current status of pesticide contamination. Therefore, the aim of this study was to determine the presence of pesticide residues in fruits and vegetables commonly consumed in Algeria and to assess the risk imposed by these residues on consumer's health.

Material and methods

Reagents

Pesticide standards of high purity were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany), Chem Service (West Chester, PA, USA) and Riedel-de Haen (Seelze, Germany). Pesticide standards used in this study were deltamethrin, lambda-cyhalothrin, cypermethrin, chlorpyrifos, metalaxyl, benalaxyl, simazine, metribuzin, tetramethrin, oxyfluorfen. Pirimiphos-methyl was used as internal standard. high performance liquid chromatography – grade acetonitrile and methanol, anhydrous $MgSO_4$ and NaCl were obtained from Sigma-Aldrich (St. Louis, MO, USA). Dispersive solid-phase extraction (DSPE) clean-up was used with pre-packed 12-ml polypropylene centrifuge tubes containing 900 mg of anhydrous $MgSO_4$ and 150 mg primary

CONTACT Samira Mebdoua mebdouasaid@yahoo.fr.

secondary amine (PSA), all purchased from Supelco (Bellefonte, PA, USA). Individual pesticide stock solutions (1000 ng μl^{-1}) were prepared in methanol or in acetonitrile and stored at −20°C. A working solution containing the mixture of standards was prepared (20 ng μl^{-1}) in acetonitrile.

Sample preparation

Representative samples (1 kg) of fresh fruits and vegetables were collected from Algerian markets and supermarkets located in Algiers, Blida and Boumerdes during 2013–2014 and chopped thoroughly using a Robot Coupe food processor (Ridgeland, MS, USA). Matrix extracts were prepared by the QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method of Anastassiades et al. (2003), according to which 10 g of homogenised sample was extracted with 10 ml of acetonitrile in 50-ml polypropylene centrifuge tubes for 1 min using manual agitation. Then 4 g anhydrous MgSO4 and 1 g NaCl were added, the tube was immediately vortexed for 1 min and centrifuged for 6 min at 2000×*g*.

DSPE clean-up was used: 4 ml of the upper layer were transferred into 12-ml centrifuge pre-packed tubes containing 150 mg PSA sorbent and 900 mg anhydrous $MgSO_4$. After vortexing for 1 min and centrifuging for 6 min at 2000 ×*g*, 1.5 ml of the purified extract was evaporated under a gentle nitrogen stream until a volume of 0.5 ml.

Analysis

For analysis, a Shimadzu (Kyoto, Japan) gas chromatography–mass spectrometry QP 5050A was used. Separation was performed on an SE 30 capillary column (50 m × 0.25 mm ID at 0.25-µm film thickness). Column temperature programme: start at 70°C, hold for 3 min, sequentially increased to 220°C at 20°C min^{-1}, hold for 11 min, increased to 282°C at 10°C min^{-1} and hold for 10 min. The carrier gas was helium (99.999%) at a column flow of 1 ml min^{-1}. The interface and the injector were programmed at 250°C for splitless injection of 1 µl. Selected ion monitoring mode with electron impact ionisation was used for the determination of selected pesticides.

Method validation and quality assurance

Quality assurance and quality control of the analytical method was performed for the following parameters: recovery, precision, linearity, limit of detection (LOD) and limit of quantification (LOQ). Assessment of recovery was performed using a mixture of the examined pesticides at fortification levels of 0.1 and 2.0 mg kg^{-1}, with five replications per level, in apple, grape, lettuce and tomato, using pesticide-free sample extracts. Precision was calculated in terms of repeatability with relative standard deviation (RSD), also by five replicated analyses at both fortification levels. To assess linearity, the extracts from blank samples were fortified with multistandard solutions of 0.01, 0.05, 0.25, 1.0 and 2.0 mg kg^{-1} and analysed in triplicate at each concentration. The LOD and LOQ were estimated as the lowest pesticide concentration producing 3 times and 10 times the signal-to-noise ratio, respectively. The reagent blank was frequently run to check any interference due to contamination from the apparatus, solvents or chemicals used. For quantification purposes, a matrix-matched calibration curve was used for apple, grape, lettuce and tomato. For other commodities, a solvent calibration curve was used. Measurement uncertainty was expressed in the database file as the RSD. Measured values between LOD and LOQ were set at LOQ/2 for calculation intake data.

Consumer exposure assessment

Assessment of chronic dietary consumer exposure was done considering both average and high pesticide residue results obtained in the analysed samples, whereas the assessment of the acute consumer dietary exposure was done only for samples containing pesticide residues above the MRLs. For the assessment of chronic consumer dietary exposure, estimated long-term dietary intake (ELTDI) and maximum long-term dietary intake (MLTDI) values were calculated and compared against relevant values of acceptable daily intake (ADI), while international estimated short-term intake (IESTI) values were calculated and compared against acute reference dose (ARfD) values, to assess acute consumer dietary exposure (World Health Organization 2009).

ELTDI and MLTDI were calculated according to the formulae:

$$\mathrm{ELTDI} = \sum \mathrm{RLi} \times \mathrm{Fi} \text{ and } \mathrm{MLTDI} = \sum \mathrm{HRi} \times \mathrm{Fi},$$

where HRi is the high residue level for a given food commodity, RLi is the average residue level for a given food commodity and Fi is the average consumption of that food commodity per person (WHO 1997). ELTDI and MLTDI were calculated for a 60-kg person and expressed as a per cent of the ADI. Food consumption data from WHO cluster diet C were used. This diet refers to 10 countries including Algeria (WHO 2006). IESTI values were calculated according to WHO guidelines (2014). Depending on food commodity, two groups were identified.

Group 1: the residue in a composite sample reflects the level in a meal-sized portion of the commodity. This case applies to commodities with a unit weight <25 g.

$$\mathrm{IESTI} = (\mathrm{LP} \times \mathrm{HR})\mathrm{bw}^{-1}$$

Group 2: meal-sized portion might have a higher residue level than the composite sample, i.e. when unit weight of a commodity is ≥25 g.

Case 2a: Unit weight U of a raw commodity is less than a large portion weight.

$$\mathrm{IESTI} = (\mathrm{U} \times \mathrm{HR} \times v + (\mathrm{LP} - \mathrm{U}) \times \mathrm{HR})\mathrm{bw}^{-1}$$

Case 2b: U is higher than a large portion weight:

$$\mathrm{IESTI} = (\mathrm{U} \times \mathrm{HR} \times \mathrm{v})\mathrm{bw}^{-1}$$

where

LP is the largest portion reported at the 97.5th percentile (kg food day^{-1}),

HR is the highest residue value (mg kg^{-1}),

Bw is the body weight (adult 60 kg, children 15 kg)

U is the unit weight of the edible portion (in kg) and

v is the variability factor which is applied to the composite residue, *v* = 7 for a unit weight between 25 and 250 g, *v* = 5 for a unit weight >250 g.

Results and discussion

Method validation and quality assurance

For all pesticides studied, recoveries were between 76% and 105%, with values of RSD less than 10%. Limits of quantification were between 0.005 and 0.05 mg kg^{-1}. Good linearity was obtained in the range 0.01–2.0 mg kg^{-1} with coefficients of correlation (R^2) higher than 0.990 (Table 1). The quality of the results was verified in each set of experiments in two ways. One was the use of a blank extract to eliminate any contamination which can result from extraction, clean-up, instruments or chemicals and the second was to check extraction efficiency by measuring recoveries at 0.1 mg kg^{-1}.

Pesticide residues in fruits and vegetables

Figure 1 shows the distribution of the analysed samples by number, origin and nature. A total of 120 samples were from domestic origin, the remaining ones were imported. The majority of the analysed samples (57.5%) were positive for at least one pesticide (Figure 2). In the analysed samples, 25.0% were positive for one, 23.1% for two, 7.5% for three and 1.9% for four or more pesticide residues. This is in accordance to many others studies. Brazilian monitoring programmes for pesticide residues in 22 fruits and vegetables showed 48.3% of samples to be positive (Jardim & Caldas 2012). In Poland, pesticide residues were found on 36.6% of analysed fruits and vegetables (Szpyrka et al. 2015). Results from Southeast Asia showed 40% of samples to be positive for at least one pesticide (Skretteberg et al. 2015). In Turkey, detectable residues were found in 62.2% of 1432 samples of fresh fruits and vegetables collected from 2010 to 2012 (Bakırcı et al. 2014). In this study, 62.9% of fruits analysed were positive for at least one residue, while only 32.1% of vegetables showed detectable residues. Similarly, Qin et al. (2015) analysed 506 vegetable samples collected from the Chinese market in the period 2010–2013. These researchers found 30.2% of the samples to contain at least one pesticide residue. In other studies, a low percentage of fruits contamination was reported. Ciscato et al. (2009) studied pesticide residues in 112 tropical fresh fruit samples in Brazil and found 23.2% to be positives. Pesticide residues monitoring in Korean fruits (Cho et al. 2009) revealed only 8.6% of pesticide residues in analysed fruits.

Pesticide residues found in this study were as follows: lambda-cyhalothrin in 63 samples, metalaxyl in 37 samples, chlorpyrifos in 35 samples, deltamethrin in 12 samples, benalaxyl in 11 samples, cypermethrin in 4 samples, tetramethrin in 2 samples and oxyfluorfen in 1 sample (Table 2). In Algeria, most insecticides authorised for use in agriculture were chlorpyrifos in 41, deltamethrin in 39, cypermethrin in 29 and lambda-cyhalothrin in 28 products. Tetramethrin was not found in any product. For fungicides, metalaxyl was authorised for 29 commercial products, while benalaxyl was registered only for 3 commercial products. Oxyfluorfen, which was the only herbicide found in this work, was authorised for nine commercial products (DPVCT 2015). The frequency of the presence of residues depending on origin is comparable in case of chlorpyrifos (domestic 21.7%; imported 22.5%), of lambda-cyhalothrin (domestic 35.8%; imported 35.0%) and of benalaxyl (domestic 6.7%; imported 7.5%). The frequency of residues in imported crops is greater than that of domestic crops in case of deltamethrin (domestic 6.7%; imported 10.0%) and cypermethrin (domestic 1.7%; imported 5.0%), while the frequency of metalaxyl in domestic crops is higher than that in imported crops (domestic 25.0%; imported 17.5%). Residues of tetramethrin and oxyfluorfen were not detected in domestic crops. For tetramethrin, this can be explained by the fact that this insecticide is not

Table 1. Parameters of the analytical method used.

Pesticide	Matrix	LOD (mg kg^{-1})	LOQ (mg kg^{-1})	R^2	Recovery and RSD (%)	Accreditation
Benalaxyl	Apple	0.006	0.02	0.9951	90.4 (5.1)	No
	Grape	0.003	0.01	0.9943	92.0 (7.1)	
	Others	0.005	0.015	0.9961	88.0 (3.6)	
	Lettuce	0.008	0.025	0.9963	91.7 (2.3)	
	Tomato	0.01	0.025	0.9955		
Chlorpyrifos	Apple	0.004	0,015	0.9993	100.1 (8.1)	No
	Grape	0.002	0.006	0.9996	105.0 (5.7)	
	Others	0.005	0.015	1.0000	95.0 (6.2)	
	Lettuce	0.005	0.015	0.9991	98.3 (7.1)	
	Tomato	0.008	0.02	0.9990		
Cypermethrin	Apple	0.008	0.02	0.9911	94.0 (4.4)	No
	Grape	0.008	0.03	0.9923	90.5 (5.1)	
	Others	0.008	0.03	0.9922	89.3 (1.9)	
	Lettuce	0.009	0.04	0.9932	87.0 (2.4)	
	Tomato	0.01	0.04	0.9919		
Deltamethrin	Apple	0.004	0.01	0.9901	88.1 (8.1)	No
	Grape	0.008	0.02	0.9917	86.2 (9.8)	
	Others	0.009	0.025	0.9922	80.6 (6.6)	
	Lettuce	0.01	0.03	0.9932	76.0 (9.3)	
	Tomato	0.005	0.015	0.9911		
Lambda-cyhalothrin	Apple	0.0008	0.005	0.9981	102.0 (3.1)	No
	Grape	0.001	0.006	0.9992	101.6 (5.6)	
	Others	0.0008	0.005	0.9991	95.9 (6.7)	
	Lettuce	0.003	0.01	0.9972	93.1 (2.9)	
	Tomato	0.002	0.008	0.9983		
Metalaxyl	Apple	0.003	0.01	0.9976	99.4 (5.5)	No
	Grape	0.001	0.008	0.9988	103.1 (5.8)	
	Others	0.004	0.01	0.9991	95.2 (7.2)	
	Lettuce	0.005	0.02	0.9967	97.6 (6.4)	
	Tomato	0.004	0.015	0.9978		
Metribuzin	Apple	0.01	0.03	0.9910	90.5 (3.1)	No
	Grape	0.008	0.02	0.9922	91.1 (2.9)	
	Others	0.01	0.03	0.9972	83.3 (4.8)	
	Lettuce	0.01	0.04	0.9931	87.2 (3.3)	
	Tomato	0.01	0.04	0.9934		
Oxyfluorfen	Apple	0.01	0.03	0.9907	90.0 (9.1)	No
	Grape	0.01	0.03	0.9919	87.6 (8.2)	
	Others	0.01	0.03	0.9922	78.1 (6.2)	
	Lettuce	0.02	0.05	0.9913	81.7 (7.1)	
	Tomato	0.02	0.04	0.9929		
Simazine	Apple	0.008	0.025	0.9934	87.2 (6.7)	No
	Grape	0.005	0.02	0.9945	85.6 (7.2)	
	Others	0.008	0.03	0.9955	80.0 (5.5)	
	Lettuce	0.01	0.04	0.9939	84.9 (4.4)	
	Tomato	0.01	0.03	0.9937		
Tetramethrin	Apple	0.0025	0.01	0.9966	104.1 (2.2)	No
	Grape	0.001	0.004	0.9976	100.5 (3.1)	
	Others	0.0008	0.005	0.9978	95.4 (5.3)	
	Lettuce	0.005	0.02	0.9979	90.0 (6.7)	
	Tomato	0.003	0.01	0.9983		

allowed in Algeria. Regarding oxyfluorfen, the absence of residues in domestic crops can be explained by the fact that Algerian farmers have no habit of using herbicides in vegetable crops and fruit trees (Kheddam-Benadjal 2012).

Table 3 shows the number and percentage of positive samples for each crop analysed. The most analysed samples were grape, apple, peach and pear, having also an important percentage of positive samples (68.4%, 59.4%, 75.0% and 66.7%, respectively). No pesticide residues were found in apricot, fig, lettuce and courgette. It should be kept in mind that the number of analysed samples is limited in this study, but gives a general view on the actual situation of these crops. The average number of pesticide residues in one positive sample ranges between 1.14 residues for potatoes and 3 residues for plums. Apples, pears, strawberries and tomatoes show an average of two residues per positive sample. The overall mean is 1.8 residues per positive sample. The higher number of pesticide residues was found in fruits: plum (7) followed by apple (6) and pear (6). A low number of pesticides were detected in vegetables: tomato (2) and potato (2). Residues of benalaxyl and metalaxyl were detected on peach, pear, apple, nectarine and plum from both domestic and imported origin. However, the use of these two fungicides is not authorised in Algeria on these fruits, so it resulted from unregulated use.

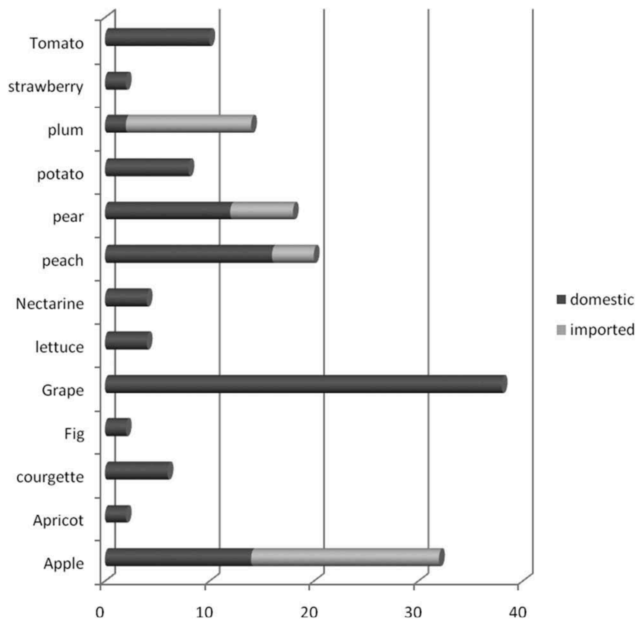

Figure 1. Distribution of the analysed samples by number, origin and nature.

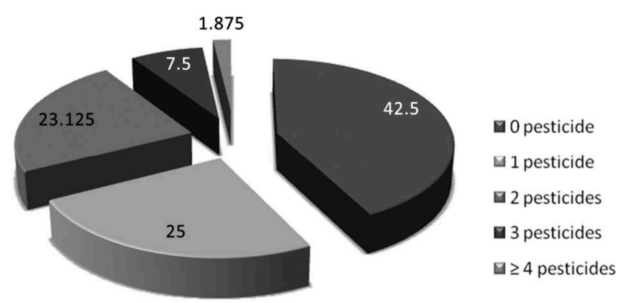

Figure 2. Number of pesticide residues in analysed samples.

In the absence of national regulation for pesticide residue levels, analytical results were compared to European and FAO/WHO MRLs. Pesticides with residue levels higher than these MRLs were chlorpyrifos in 12 samples, lambda-cyhalothrin, deltamethrin and metalaxyl in 4 samples, benalaxyl in 2 samples and oxyfluorfen in 1 sample (Table 2). Peach was the crop with the highest number of samples with residues above MRL, exclusively from domestic origin (Table 3), due to chlorpyrifos (five samples) and metalaxyl (two samples). Nectarine showed the highest percentage of samples with residues above MRLs (50%), also from domestic origin only. Apple represented 12.5% of its samples above MRLs only from domestic origin due to benalaxyl (two samples) and chlorpyrifos, deltamethrin and lambda-cyhalothrin multi-residues (two samples).

The percentage of samples with residues exceeding MRLs in this study (12.5%) was higher than the majority of those reported in many others studies. Less than 3% of samples had residues above the MRLs in Brazilian monitoring programmes of pesticide residues (Jardim & Caldas 2012). The United States Food and Drug Administration (US FDA) stated that violations were detected in 2% of the domestic and 7% of the imported vegetable samples and only in 4.8% of imported fruit samples (Winter 2012). For the European monitoring programme for pesticides, a total of 11,610 samples of nine different commodities (oranges, mandarins, pears, potatoes, carrots, cucumbers, spinach, beans and rice) were analysed for residues of 78 specific pesticides, of which 35.7% contained legal residues and 2.2% exceeded MRLs (Winter 2012). Szpyrka et al. (2015) found 1.8% exceedance of MRLs in fruits and vegetables analysed in Poland. However, our findings were better than those reported for some Asian countries. For example, in Pakistan, Parveen et al. (2011) studied apple, apricot, persimmon, chiku, citrus, grapes, guava, mango, papaya, peach, plum, melon, banana and pomegranate samples procured from different selling points of Karachi during 2008–2009 and reported that about 22% of the total samples exceeded the MRLs. A study from India (Swarnam & Velmurugan 2013) found that 15% of vegetable samples tested contained pesticide residues that exceeded the MRLs. In addition, the incidence of pesticides above MRL was reported to be 24% in various vegetables collected

Table 2. Pesticide residues detected in analysed samples.

Pesticide	*N* > LOD (%)	*N* > MRL (%)	Range (mg kg^{-1})	Positive crop (*N* > LOD)
Benalaxyl	11 (6.9)	2 (1.3)	0.016–0.181	Apple (2), plum (3), pear (1), peach (3), tomato (2)
Chlorpyrifos	35 (21.9)	12 (7.5)	0.053–9.830	Apple (12), grape (10), nectarine (2), plum (1), pear (2), peach (5), potato (1), strawberry (2)
Cypermethrin	4 (2.5)	0	0.033–0.599	Apple (2), plum (2)
Deltamethrin	12 (7.5)	4 (2.5)	0.01–0.416	Apple (5), nectarine (1), plum (2), pear (3), peach (1)
Lambda-cyhalothrin	63 (39.4)	4 (2.5)	0.0025–0.260	Apple (16), grape (10), nectarine (4), plum (5), pear (12), peach (7), potato (7), strawberry (2)
Metalaxyl	37 (23.1)	4 (2.5)	0.004–0.412	Apple (1), grape (18), nectarine (3), plum (1), pear (4), peach (8), tomato (2)
Oxyfluorfen	1 (0.6)	1 (0.6)	0.089	Plum (1)
Tetramethrin	2 (1.3)	0	0.0177–0.0288	Pear (2)

Table 3. Results obtained from analysed samples.

Crop	N	N > LOD (%)	N > MRL (%)	Identified pesticides
Apple	32	19 (59.4)	4 (12.5)	Benalaxyl, chlorpyrifos, cypermethrin, deltamethrin, lambda-cyhalothrin, metalaxyl
Apricot	2	0	0	
Courgette	6	0	0	
Fig	2	0	0	
Grape	38	26 (68.4)	2 (5.3)	Chlorpyrifos, lambda-cyhalothrin, metalaxyl
Lettuce	4	0	0	
Nectarine	4	4 (100)	2 (50.0)	Chlorpyripfs, deltamethrin, lambda-cyhalothrin, metalaxyl
Peach	20	15 (75.0)	7 (35.0)	Benalaxyl, chlorpyrifos, deltamethrin, lambda-cyhalothrin, metalaxyl
Pear	18	12 (66.7)	2 (11.1)	Benalaxyl, chlorpyrifos, deltamethrin, lambda-cyhalothrin, metalaxyl, tetramethrin
Plum	14	5 (35.7)	1 (7.1)	Benalaxyl, chlorpyrifos, cypermethrin, deltamethrin, lambda-cyhalothrin, metalaxyl,oxyfluorfen
Potato	8	7 (87.5)	2 (25.0)	Chlorpyrifos, lambda-cyhalothrin
Strawberry	2	2 (100)	0	Chlorpyrifos, lambda-cyhalothrin
Tomato	10	2 (20.0)	0	Benalaxyl, metalalxyl

from markets in the northern region of Thailand (Sapbamrer & Hongsibsong 2014).

Risks assessment

Chronic risk assessment requires determination of the estimate of daily exposure. Two factors need to be considered: pesticide residue concentrations on food and the rate of consumption. In general, long-term exposure of the Algerian consumer to pesticide residues through consumption of raw fruit and vegetables appeared to be low (Table 4). The highest exposure was observed for chlorpyrifos (42% of ADI when using HR, 2% of ADI when using average residue level [LR]) followed by lambda-cyhalothrin (3% of ADI when using HR, 0.5% of ADI when using LR). In most cases, pesticide exposure was below 1% ADI. Our results showed a negligible risk associated with the exposure via fruit and vegetables consumption. A special precaution should be taken with the possible aggregate exposure to chlorpyrifos from other sources of nutrition such as grain, other fruits and vegetables, water and juices. Chlorpyrifos is an organophosphorus insecticide with a large spectrum activity. It acts by cholinesterase inhibition, which is the cause of potential toxicity in humans. This mode of action is common to organophosphorus and carbamate insecticides and acaricides. There is a rising need to study the cumulative long-term risk assessment of these organophosphorus and carbamate insecticides. In Algeria, chlorpyrifos, fenitrothion, diazinon, dimethoate, omethoate, dichlorvos, pirimiphos-methyl, parathion methyl, carbosulfan, methomyl, oxamyl and pirimicarb are authorised (DPVCT 2015).

Table 4. Long-term risk assessment (intake expressed as µg kg^{-1} bw^{-1} and ADI as mg kg^{-1} bw^{-1}).

Pesticide	ADI	MLTDI	% of ADI	ELTDI	% of ADI
Chlorpyrifos	0.01	4.238	42.4	0.235	2.35
Lambda-cyhalothrin	0.005	0.1672	3.34	0.0242	0.49
Deltamethrin	0.01	0.0882	0.88	0.0086	0.09
Metalaxyl	0.08	0.5894	0.74	0.0915	0.11
Cypermethrin	0.02	0.1864	0.93	0.0079	0.04
Benalaxyl	0.07	0.0031	0.00	0.0003	0.00
Tetramethrin	0.02	0.0013	0.01	0.0001	0.00
Oxyfluorfen	0.003	0.0036	0.12	0.0003	0.01

A chronic pesticide exposure study from the US FDA regulatory monitoring programme showed that in most cases chronic exposure to pesticides from fruits and vegetables was less than 2% of ADI. Pesticides for which exposure estimates were larger than 2% of ADI were as follows: permethrin, acephate, methamidophos and dichloran (Katz & Winter 2009). In this direction, Knežević et al. (2012) evaluated the risk of long-term dietary intake of pesticides in the Croatian diet. They found in most cases exposure to be in the range of 0.02–4% of ADI. The highest exposure was observed for diazinon (70% of ADI). Relatively high exposure was observed for methidathion (13% of ADI), chlorpyrifos (10% of ADI) and Imazalil (10% of ADI).

The assessment of acute (short-term) exposure is based both on extreme food consumption and the highest residue level detected. In this study, acute exposure was calculated only for pesticides exceeding the MRLs. Assuming the coincidence of these events, a potential consumer short-term risk was identified for five pesticide/commodity combinations for children (chlorpyrifos/apple, chlorpyrifos/grapes, lambda-cyhalothrin/apple, deltamethrin/apple, deltamethrin/pear) and for two pesticide/commodity combinations (chlorpyrifos/apple, deltamethrin/pear) for the adult population (Table 5). The values of short-term exposure ranged between 0.78% and 558.5% of ARfD for children and between 0.23% and 237.8% of ARfD for adults. In a similar study, Knežević et al. (2012) identified a potential acute exposure for eight pesticide/commodity combinations for the population of Croatian children (>150% of ARfD) and three pesticide/commodity combinations for the population of Croatian adults (>150% of ARfD). Combinations with the highest ARfD exceedances were as follows: Imazalil/orange, tolylfluanid/apple and azinphos-methyl/peach. In a study of short-term intake of pesticide residues in fruits and vegetables from South Eastern

Table 5. Short-term risk assessment (intake and ARfD expressed as mg kg^{-1} bw^{-1}).

Pesticide residue	Crop	ARfD	HR	IESTI Children	% of ARfD	IESTI Adult	% of ARfD
Chlorpyrifos	Peach	0.1	0.747	0.0472	47.2	0.0138	13.8
	Apple		9.830	0.5585	558.5	0.2378	237.8
	Grape		1.978	0.1477	147.8	0.0394	39.4
	Potato		0.215	0.0194	19.4	0.0065	6.5
	Nectarine		0.785	0.0501	50.1	0.0147	14.7
Lambda-cyhalothrin	Apple	0.0075	0.260	0.0147	196.0	0.0063	83.87
	Potato		0.039	0.0035	46.9	0.0012	15.83
Deltamethrin	Pear	0.01	0.416	0.0408	407.8	0.01137	113.7
	Apple		0.208	0.0118	118.2	0.0050	50.3
Metalaxyl	Nectarine	0.5	0,061	0.0039	0.78	0.00114	0.23
	Peach		0.155	0.0099	1.98	0.00291	0.58
Benalaxyl	Apple	0.1	0.102	0.0058	5.79	0.0025	2.47
Oxyfluorfen	Plum	0.3	0.089	0.0045	1.51	0.0014	0.46

Poland, Szpyrka et al. (2015) did not observe exceedances of 100% of the ARfD.

Conclusion

The present study shows that 57.5% of fruit and vegetable samples collected from Algerian markets contained at least one pesticide residue. Exceedance of MRLs was observed in 12.5% of analysed samples, concerning chlorpyrifos, lambda-cyhalothrin, deltamethrin, metalaxyl, benalaxyl and oxyfluorfen. Risk assessment for long-term exposure was done for all pesticides detected. Except chlorpyrifos and lambda-cyhalothrin, exposure to pesticides from vegetables and fruits was below 1% of the ADI. For short-term risk assessment, exceedance of 100% of the ARfD was identified for seven pesticide/commodity combinations, including only three pesticide residues: chlorpyrifos, deltamethrin and lambda-cyhalothrin. This study was limited to only 13 types of crops and 10 pesticides, which is insufficient to assess a total exposure to pesticides through food. Therefore, monitoring of more pesticide residues in a greater variety of crops should be developed in order to guarantee food intake according to international food safety standards for the Algerian consumer.

Acknowledgement

The authors would like to thank the National Institute of Plant Protection (INPV) for providing pesticide standards.

Disclosure statement

No potential conflict of interest was reported by the authors.

References

[DPVCT] Direction de la Protection des Végétaux et Contrôles Techniques. 2015. Index des produits phytosanitaires à usage agricole. [Index of phytosanitary products for agricultural use]. Alger: Ministère de l'Agriculture et du Développement Rural. [Internet]. [cited 2016 Jan 20]. Available from: http://www.inpv.edu.dz/institut/wp-content/uploads/2016/03/INDEX_PRODUITS_PHYTO_2015.pdf

[WHO] World Health Organization. 1997. Guidelines for predicting dietary intake of pesticide residues (revised). [Internet]. [cited 2016 Jan 20]. Available from: http://www.who.int/foodsafety/publications/chem/en/pesticide_en.pdf.

[WHO] World Health Organization. 2006. The GEMS/Food consumption cluster diets [Internet]. [cited 2016 Jan 20]. Available from: http://www.who.int/foodsafety/chem/ClusterDietsAug06.xls

[WHO] World Health Organization. 2009. Principles and methods for the risk assessment of chemicals in food. Chapter 6, Dietary exposure assessment of chemicals in food. Environmental Health Criteria, No. 240 [Internet]. FAO/WHO International programme on chemical safety. Geneva: WHO. [cited 2016 Jan 20]. Available from: http://apps.who.int/iris/bitstream/10665/44065/9/WHO_EHC_240_9_eng_Chapter6.pdf

[WHO] World Health Organization. 2014. International estimated short-term intake (IESTI) [Internet]. [cited 2016 Jan 20]. Available from: http://www.who.int/foodsafety/chem/guidance_for_IESTI_calculation.pdf

Anastassiades M, Lehotay SJ, Štajnbaher D, Schenck FJ. 2003. Fast and easy multiresidue method employing acetonitrile extraction/partitioning and "dispersive solid-phase extraction" for the determination of pesticide residues in produce. J AOAC Int. 86:412–431.

Bakırcı GT, Acay DBY, Bakırcı F, Ötleş S. 2014. Pesticide residues in fruits and vegetables from the Aegean region, Turkey. Food Chem. 160:379–392.

Cho TH, Kim BS, Jo SJ, Kang HG, Choi BY, Kim MY. 2009. Pesticide residue monitoring in Korean agricultural products, 2003–05. Food Addit Contamin B. 2:27–37.

Ciscato CHP, Amir Bertoni Gebara AB, Monteiro SH. 2009. Pesticide residue monitoring of Brazilian fruit for export 2006–2007. Food Addit Contamin Bsurveil. 2:140–145.

Jardim ANO, Caldas ED. 2012. Brazilian monitoring programs for pesticide residues in food – Results from 2001 to 2010. Food Control. 25:607–616.

Juraske R, Antón A, Castells F, Huijbregts MAJ. 2007. Human intake fractions of pesticides via greenhouse tomato consumption: comparing model estimates with measurements for Captan. Chemosphere. 67:1102–1107.

Karmas E, Harris RS, editors. 1988. Nutritional evaluation of food processing. New York (NY): Van Nostrand Reinhold.

Katz JM, Winter CK. 2009. Comparison of pesticide exposure from consumption of domestic and imported fruits and vegetables. Food Chem Toxicol. 47:335–338.

Kheddam-Benadjal N. 2012. Enquête sur la gestion des pesticides en Algérie et recherche d'une méthode de lutte alternative contre *Meloidogyne incognita* (Nematoda: meloidogynidae) [Investigation on pesticide management in Algeria and research of an alternative method to control *Meloidogyne incognita* (Nematoda: meloidogynidae)]. Alger: Ecole Nationale Supérieure Agronomique (ENSA).

Knežević Z, Serda M, Ahel M. 2012. Risk assessment of the intake of pesticides in Croatian diet. Food Control. 23:59–65.

Nasreddine L, Parent-Massin D. 2002. Food contamination by metals and pesticides in the European Union. Should we worry? Toxicol Lett. 127:29–41.

Parveen Z, Riazuddin Iqbal S, Khuhro MI, Bhutto MA, Ahmed M. 2011. Monitoring of multiple pesticide residues in some fruits in Karachi, Pakistan. Pak J Bot. 43:1915–1918.

Prodanov M, Sierra I, Vidal-Valverde C. 2004. Influence of soaking and cooking on the thiamin, riboflavin and niacin contents of legumes. Food Chem. 84:271–277.

Qin G, Li Y, Chen Y, Sun Q, Zuo B, He F, Shen N, Jia G, Ding G. 2015. Pesticide residues determination in China vegetables in 2010–2013 applying gas chromatography with mass spectrometry. Food Res Int. 72:161–167.

Sapbamrer R, Hongsibsong S. 2014. Organophosphorus pesticide residues in vegetables from farms, markets, and a supermarket around Kwan Phayao Lake of Northern Thailand. Arch Environ Contam Toxicol. 67:60–67.

Skretteberg LG, Lyrån B, Holen B, Jansson A, Fohgelberg P, Siivinen K, Andersen JH, Jensen BH. 2015. Pesticide residues in food of plant origin from Southeast Asia - A Nordic project. Food Control. 51:225–235.

Swarnam TP, Velmurugan A. 2013. Pesticide residues in vegetable samples from the Andaman Islands, India. Environ Monit Assess. 185:6119–6127.

Szpyrka E, Kurdziel A, Matyaszek A, Podbielska M, Rupar J, Słowik-Borowiec M. 2015. Evaluation of pesticide residues in fruits and vegetables from the region of south-eastern Poland. Food Control. 48:137–142.

Winter CK. 2012. Pesticide residues in foods. In: Schrenk D, editor. pesticide residues in foods. Amsterdam: Elsevier; p. 183–200. doi:10.1533/9780857095794.2.183